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HYDROGEN STORAGE IN THE FORM OF METAL HYDRIDES

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| 16. Abstract Reversible reactions between hydrogen and such materials as iron/titanium and magnesium/ nickel alloy may provide a means for storing hydrogen fuel. In this paper, a demonstration model of an iron/titanium hydride storage bed is described. Hydrogen from the hydride storage bed powers a converted gasoline electric generator. | | | | | |
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SUMMARY One of the critical aspects of hydrogen technology is the storage of this raw material for later use. The reversible chemical reactions between hydrogen and metallic alloys are a promising avenue of research. The idea has been tested in practical applications by several laboratories with iron/titanium, magnesium/nickel and lanthanum/nickel systems, to mention a few. We demonstrate an iron/titanium hydride bed that feeds hydrogen to a converted gasoline motoelectric generator.
(Authors' summary)

*

1. INTRODUCTION

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Currently there are various research centers, world-wide, that are studying the feasibility of hydrogen storage in the form of hydrides, whose energies of formation and dissociation are reversible, with kinetic and thermodynamic characteristics (in addition to energy density and cost) suitable for practical applications.

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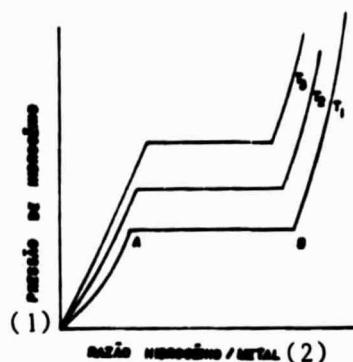
Considerable progress was achieved during the last decade and the technical feasibility of fuel tanks for automobiles has already been shown by various companies, such as Billings, in the US and Daimler-Benz, in West Germany.

In Brazil there is the possibility and hope of producing electrolytic hydrogen from the still fairly abundant hydroelectric power reserves. As a traditional market technology, the cost of energy to the consumer - in the form of electrolytic hydrogen - is comparable to petroleum-based fuel costs, at current price schedules. Under these conditions it is reasonable to consider hydrogen operation for fleets of heavy freight transports, traveling between certain destinations, to minimize supply problems. The basic point of the entire matter is the storage, and here metal hydride tanks are a practical and safe alternative.

2. PHYSICOCHEMICAL ASPECTS

Metal hydrides are compounds formed by the reaction between metals and metal alloys and hydrogen. The metal hydride formation reactions of interest are exothermal, with the heat removed providing a measure of the quantity of hydrogen absorbed. At a given temperature, each system is in equilibrium with a certain hydrogen pressure, called the equilibrium pressure. The reaction is reversible, which made these systems attractive as possible hydrogen storage devices. The pressures involved are moderate (a few Kgf/cm^2) and the process is safe, since it is necessary to supply thermal energy to obtain hydrogen. Hydrogen densities in terms of hydrogen atoms per unit volume are higher even than those for liquid hydrogen, as shown in Table 2 of reference 2.

The equilibrium pressure is a function of the temperature and of the hydrogen concentration in the solid phase. Figure 1, /544



KEY: 1. Hydrogen pressure 2. Hydrogen/metal ratio

Figure 1. Pressure isotherms as a function of composition for ideal metal-hydrogen systems

above, shows the typical behavior of metal-hydrogen systems.

As hydrogen is absorbed at constant temperature T_1 and the hydrogen/metal ratio increases, the equilibrium pressure rises sharply, to point A. During this period the solid consists of a solution of hydrogen atoms in the metal, but not a different compound. From point A on, the increase in hydrogen concentration causes no further increase in the equilibrium pressure; X-ray analysis shows that the solid consists of a mixture of metal + metal hydride, with the proportion of the latter increasing until all the metal has become metal hydride, a state described by point B, in Figure 1. From point B on, we have a solution of hydrogen in the metal hydride, with a typical increase in pressure as a function of the composition. In some systems (for instance, in the iron-titanium alloy), yet a second plateau can be observed, at a higher pressure level.

The curves marked T_2 and T_3 show the effect of temperature ($T_1 < T_2 < T_3$). Figure 2, below, shows the dissociation pressures as a function of temperature, for some systems.

One system of practical interest, despite its high density, is

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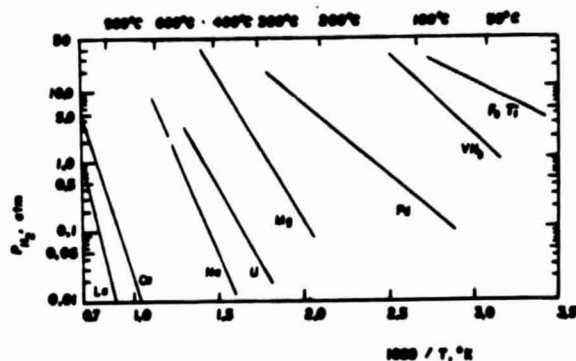
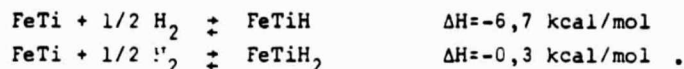


Figure 2. Dissociation pressures for hydrides of some metals and alloys

that of the iron-titanium alloys, due to its low costs and moderate equilibrium pressure [1].

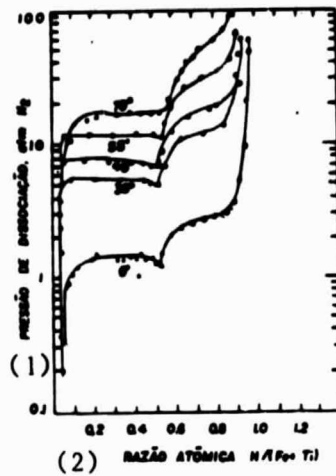
The equiatomic intermetallic compound FeTi (46.4% Ti by weight, /545 53.6% by weight iron) reacts reversibly with hydrogen to form hydrides according to the reactions



The reaction products are solids of metallic appearance, gray, fragile, readily reduced to powder, not pyrophoric and release hydrogen only slowly to the air.

The variation of the equilibrium pressure as a function of the hydrogen content is shown in Figure 3 (from [1]), for various temperatures. The FeTiH system has also a characteristic hysteresis effect in the absorption/desorption process.

Some advances in the physical chemistry of hydrate formation, including the effect of additional chemical elements to the alloys, are described in [3-6].



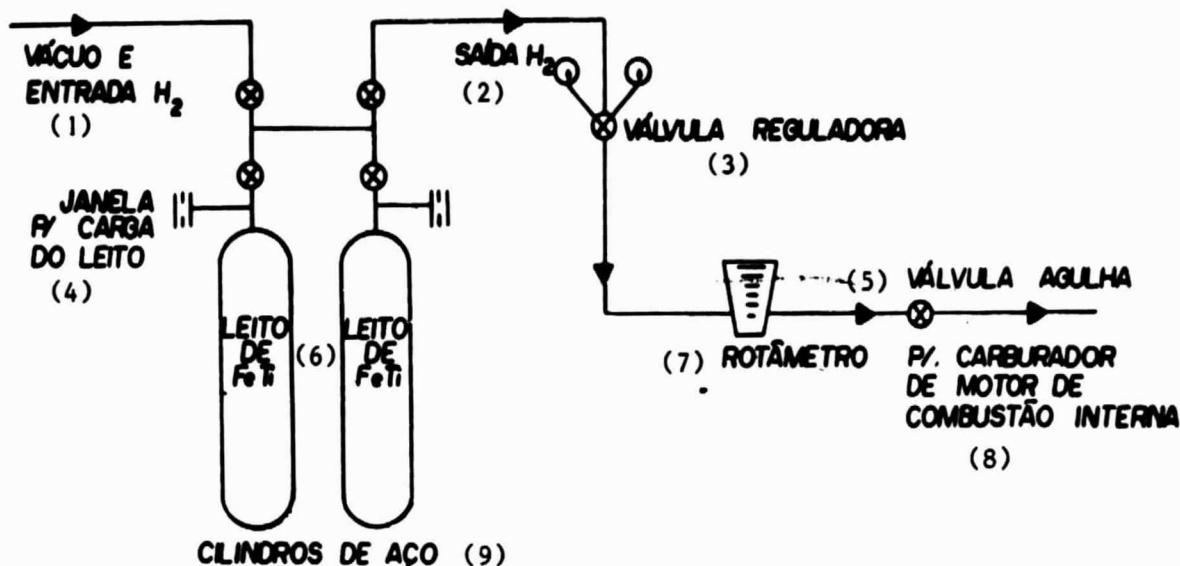
KEY: 1. Dissociation pressure 2. Atomic ratio

Figure 3. Pressure as a function of composition isotherms for stoichiometric FeTi hydrides

3 STORAGE TANKS FOR H_2 IN HYDRIDE FORM

In order to test the utilization of hydride tanks for energy-generation purposes, a demonstration unit was built. A FeTi alloy was used, prepared at UNICAMP in an electron beam furnace and activated in the storage tank itself. A quantity of 2.7 kg of the alloy were placed in a storage tank formed by two steel cylinders with a combined capacity of 0.8 l, connected to a Montgomery generator group of 3.6 V mechanical power with the carburetor removed. Hydrogen was injected directly into the admission tube. The storage capacity achieved was 250 normal liters of hydrogen at an equilibrium pressure of 15 kgf/cm^2 . This quantity is half the ideal quantity because a non-stoichiometric alloy was used.

The power is regulated by means of a needle valve on the hydrogen line. The motor was not modified in any other way. Under these conditions, the thermodynamic energy conversion yield is necessarily rather poor, but the device functioned normally and /547



KEY: 1-Vacuum and H₂ admission 2-H₂ exit 3-Regulator valve 4-Bed loading window 5-Needle valve 6-FeTi bed 7-Flow meter 8-To the carburetor of an internal combustion engine 9-Steel cylinders

Figure 4. Hydride tank - demonstration unit

without problems.

Figure 4, above, shows a schematic of the assembly.

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